Supplemental Material: Structural modification of thin Bi(1 1 1) films by passivation and native oxide model

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STABILITY OF THE HYDROGEN AND HYDROXYL TERMINATED SURFACES

The stability of the terminated surfaces depends on the chemical potentials μ_i of the involved reactants i which can be controlled in the experiment by adjusting the temperature and the gas pressure (e.g. of H_2). We employ a formalism similar to Refs. [1, 2] where the Gibbs free energy G is approximated by the DFT total energy and vibrational contributions are neglected for the terminated slab. The formation energy is then given by

$$E^{\text{formation}} = G - \sum_i N_i \mu_i \ , \tag{1}$$

$$\approx E^{\text{DFT}} + pV - \sum_i N_i \mu_i \ . \tag{2}$$

with the particle numbers N_i. The surface free energy γ is then the difference between the formation energies of the terminated system and the unterminated slab divided by the surface area A. Both systems need to have the same number of particles which can be achieved by additional gas molecules in the vacuum. Let γ_x be the surface free energy of a system terminated with x hydrogen atoms per surface atom. The orthorhombic slab has two surface atoms on each side, therefore

$$\gamma_x\left(T, p_{\text{H}_2}\right) = \left[E_x^{\text{DFT}} - E_{x=0}^{\text{DFT}} - 4x\mu_{\text{H}}\left(T, p_{\text{H}_2}\right)\right]/A \ . \tag{3}$$

By assuming that the chemical potential of a single H atom at 0 K is half of the DFT energy of a H_2 molecule, we can make the ansatz

$$\mu_{\text{H}} = \frac{1}{2}\left(E_{\text{H}_2}^{\text{DFT}} + \Delta\mu_{\text{H}_2}\left(T, p_{\text{H}_2}\right)\right) \ , \tag{4}$$

$$\text{where} \quad \Delta\mu_{\text{H}_2}\left(0\,\text{K}, p_{\text{H}_2}\right) = 0 \ . \tag{5}$$

The chemical potential can be interpreted as a parameter in the theoretical considerations and the results are shown in Fig. 1(a). Apparently, the terminations are not stable at 0 K corresponding to $\Delta\mu_{\text{H}_2} = 0$ and the chemical potential has to increase by more than 1 eV to obtain a stable structure. However, in the DFT calculation the hydrogen atoms on the surface are too far apart to react with each other during the atomic relaxation. The bonds to the film show that the termination is stable with respect to single hydrogen atoms.

Following the reasoning in Refs. [1, 2], assuming an ideal gas it can be shown by calculating the total derivative of μ that with respect to 0 K and an arbitrary pressure p_0

$$\Delta\mu(T,p) = \left.\frac{H - ST}{N}\right|_{0K,p_0}^{T,p_0} + kT\ln\left(\frac{p}{p_0}\right) \ . \tag{6}$$

Note that $\Delta\mu = 0$ for 0 K independent of the pressure which is why p_0 is arbitrary. Experimental values for the enthalpy H and entropy S can be found in the literature [3] for atmospheric pressure (1 atm or 1013.25 hPa). Fig. 1(b) shows how the chemical potential of H_2 changes with temperature and gas pressure. We find that the changes of μ_{H_2} which would be necessary to stabilize the surface are only accessible with very high pressure.

The same considerations can be applied to the hydroxyl termination. We assume that water reacts with the surface of the bismuth films which leads to the formation of H_2. Thus, there are two chemical potentials μ_{H_2} and $\mu_{\text{H}_2\text{O}}$ which have to be taken into account. In line with the paper we restrict our discussion here to a single OH per surface atom. Fig. 2(a) shows the surface free energy as a function of the chemical potentials. The influence of the experimental control parameters on $\mu_{\text{H}_2\text{O}}$ are displayed in Fig. 2(b). Again, under the assumptions made, we find that the structure is not stable under typical experimental conditions. We stress however that the terminations above should rather be considered as model systems with a specified amount of covalent bonds to the surface.

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[2] K. Reuter and M. Scheffler, "First-principles atomistic thermodynamics for oxidation catalysis: Surface phase diagrams and catalytically interesting regions," Phys. Rev. Lett. **90**, 046103 (2003).
[3] D. R. Stull and H. Prophet, *JANAF thermochemical tables*, 2nd ed. (National Bureau of Standards (U.S.), Washington, D.C., 1971).

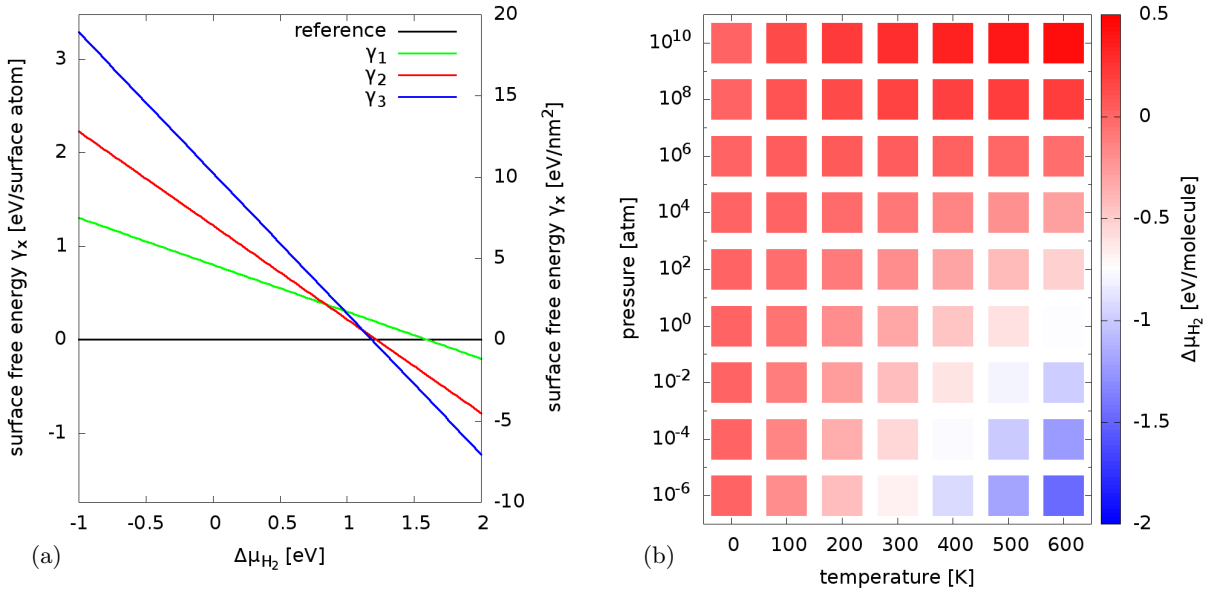

Figure 1. (a) Stability of the surfaces terminated with x hydrogen atoms per surface atom as a function of changes of the chemical potential of the hydrogen gas with respect to 0 K. The error introduced by basis set superposition is negligible (approximately 1 %). (b) Dependence of $\Delta\mu_{H_2}$ on pressure and temperature. We find that the terminated surfaces are only stable if the chemical potential of the hydrogen gas can be substantially increased. This corresponds to a very high gas pressure exceeding typical experimental conditions.

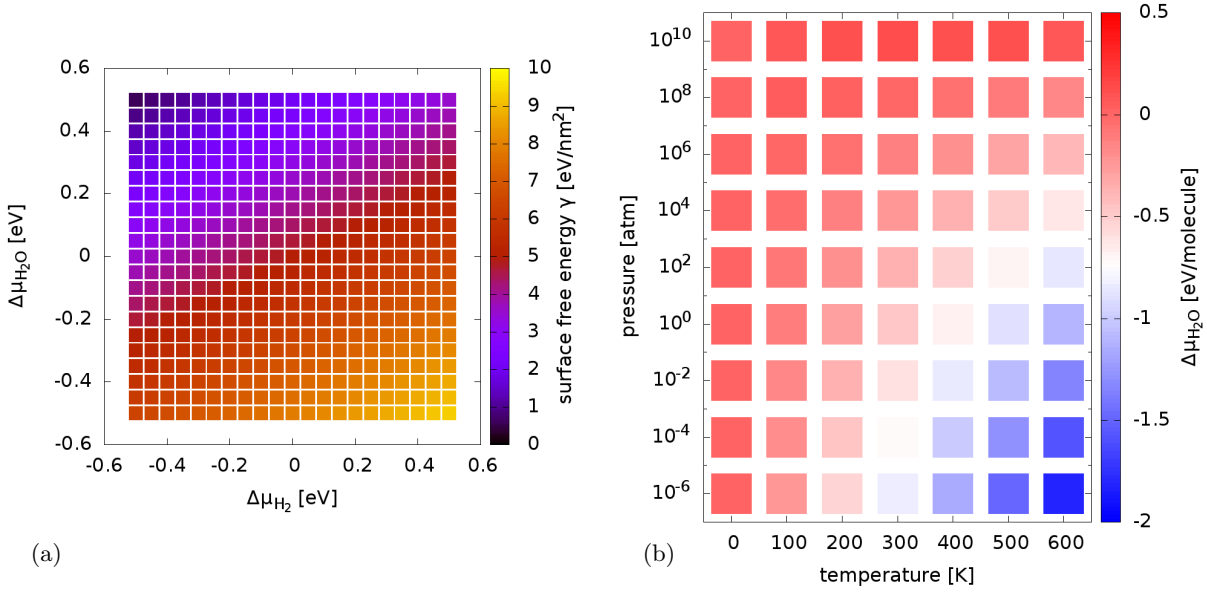

Figure 2. (a) Stability of the OH-terminated surface (one OH per surface atom) as a function of changes of μ_{H_2} and μ_{H_2O} with respect to 0 K. Water molecules are assumed to dissociate at the surface, leading to a passivated surface and the formation of H_2. At $\Delta\mu_{H_2} = \Delta\mu_{H_2O} = 0$ we find $\gamma = 4.95\,\mathrm{eV/nm^2}$. (b) Dependence of $\Delta\mu_{H_2O}$ on pressure and temperature. The terminated surface is not stable under typical experimental conditions as we have already observed for the hydrogen terminated surfaces.